III.A.15 Reliable Seals for Solid Oxide Fuel Cells

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Objectives

- Develop reliable, cost-effective sealing techniques for solid oxide fuel cells (SOFCs).
- Determine performance-limiting features of sealing methods.
- Optimize seal properties.
- Determine seal degradation mechanisms and predict useful seal lifetimes.

Approach

- We are making glass matrix composite seals with a wide range of chemical and mechanical properties.
- The composite approach allows glass and filler properties to be optimized independently.
- Seal thermal and mechanical strains are reduced by selecting glass compositions with glass transition temperatures (T_gs) below the SOFC operating temperature.
- Viscosity, coefficient of thermal expansion (CTE), and other seal characteristics can be tailored by adding unreactive powder.
- The volume fraction of the glass phase can be reduced to a minimum for the seal, which reduces reactivity with fuel cell materials.

Accomplishments

- We modified our glass compositions to provide better control over flow and thermal expansion properties.
- Glass sealants exhibit little or no reactivity with SOFC anode materials at 750-800°C. Glass seal compositions show little or no reactivity with stainless steel interconnect materials at 750°C.
- Preoxidizing interconnect materials enhances glass wetting and adhesion required for sealing.

Future Directions

- Develop screening test for adhesion of different seal compositions and processes.
- Conduct further tests of effects of environmental exposure on seal properties.
- Refine reaction studies of sealants with SOFC components.
- Perform more fundamental mechanical tests on composite seal materials at operating temperatures; e.g., flexural strength and fracture toughness.
- Investigate shaping and forming methods for composite seals such as tape casting and screen printing

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Introduction

Developing reliable methods for sealing solid oxide fuel cell stacks presents the most challenging set of performance criteria in the entire field of ceramic joining. For SOFC applications, the requirements on the sealing method include:

- adhesion of the sealing material to fuel cell components from room temperature to as high as 1000°C

- ability to provide a leak-tight seal at the SOFC operating temperature
- ability to maintain a seal while accommodating strains from SOFC components with different coefficients of thermal expansion (CTEs)
- lack of adverse reaction between the sealing material(s) and the fuel cell components
- chemical and physical stability of the sealant at temperatures up to 1000°C in oxidizing and reducing atmospheres
- thermal shock tolerance
- electrically insulating for some SOFC designs

All of the above properties must be maintained for SOFC operating lifetimes of up to 40,000 hours. The list is written in approximate order of decreasing stringency. That is, no matter what the SOFC design, the seal must be adherent and leak-tight. On the other hand, some stack designs may require joining only similar materials and, thus, a matched CTE seal may be sufficient. Note also that the requirements may be contradictory. For example, being leak-tight and adherent at high temperatures suggests a refractory, stiff sealant, which may work against the requirement for thermal strain accommodation. Such situations are common, and seal developers know that seal design is specific to a particular component geometry and usually requires compromises among competing requirements.

Approach

Under DOE sponsorship, this project is developing an approach to sealing SOFCs that can be tailored to the specific requirements of the vertical teams in the DOE/SECA (Solid State Energy Conversion Alliance) program. The technique combines extensive capabilities in ceramic joining and composites that have been developed at Sandia over the past 20 years. In our judgment, relief of thermal expansion mismatch stresses will require SOFC seals to incorporate either a ductile metal or a high-viscosity glass that can relieve stresses through viscous creep. Other design and operational constraints on SOFCs, which as discussed above frequently are in opposition, severely restrict the options for seal materials. Based on our prior experience in ceramic joining and on results obtained so far on this project, we believe we have greatest design flexibility using ceramic-filled glasses and metal-filled glass composites. We have demonstrated that we can control properties such as glass transition temperature and thermal expansion coefficient by varying the compositions, amounts, and microstructures of the different phases. The choices are guided by thermochemical and composite microstructural models that allow us to target specific seal properties for a given design. Several seal systems are showing promise in functional tests.

Results

We have shown that our SOFC sealing technique can be tailored to fit a wide range of SOFC specifications. The essence of the method is to engineer ceramic-filled glass composites, metal-filled glass composites, and/or ceramic-filled metal composites that can meet SOFC requirements. This approach combines extensive capabilities in composites and ceramic joining that have been developed by Sandia National Laboratory staff over the past 15 - 20 years.

The composite seals require a glass matrix that is slightly fluid at the SOFC operating temperature to reduce thermal strains. In technical terms, this requires a glass transition temperature that is below the cell operating temperature. Our compositional modifications vary the glass T_gs and expansion coefficients and thus give us a wider choice of matrix materials for our composite seals. The flow properties are reflected as differences in the rate of spreading of a molten glass drop on the substrate of interest. For example, a more fluid glass at a given temperature will spread faster and assume a lower contact angle than one that is less fluid. In a recent series of tests at 750°C, ten glass compositions exhibited a range in contact angles after 5 minutes on 410 stainless steel (a typical SOFC alloy) from 80° (low flow, poorer wetting) to 20° (faster flow, good wetting). No one glass is necessarily better than another for all use conditions. Rather, the results demonstrate that our glasses span a wide range of physical properties, which allows us a lot of options in engineering optimized SOFC seals (Figure 1).

Constructing SOFC stacks may require seals to Ni – YSZ (yttria-stabilized zirconia) anodes. Thus, we tested different glasses for reactivity using a

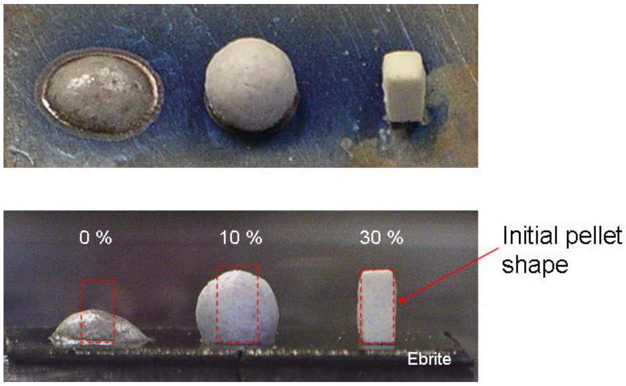

Figure 1. Top and side views of sealants heated on Ebrite stainless steel for 10 min at 850°C. Sealants are Glass 14a with indicated volume fraction of YSZ powder. The seal wetting and flow properties are controlled by the glass-powder ratio.

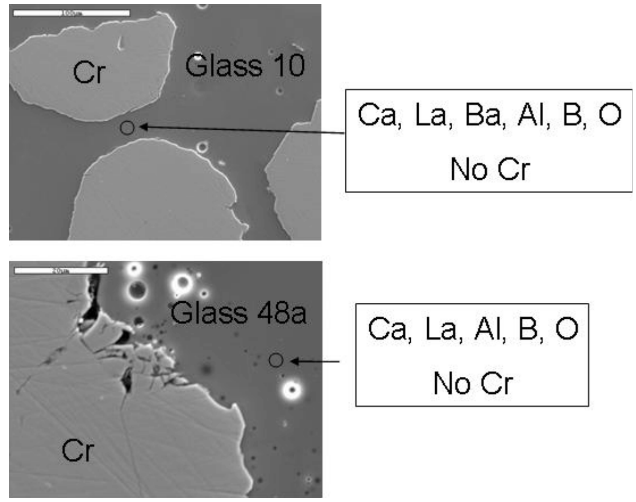

Figure 2. Glass-Cr Powder Composites Heated for 3 hr at 750°C Show No Evidence of Cr Dissolution in the Glass

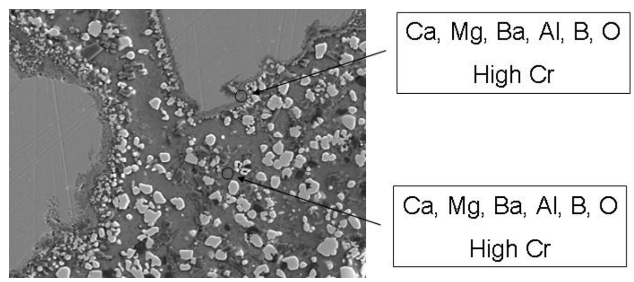

Figure 3. Glass-Cr Composites Heated at 850°C Show Cr_2O_3 Layer on Cr Particles and Cr Dissolution in the Glass

sessile drop test geometry in which small glass specimens were heated on anode material for different times at fixed temperature. During heating, we monitored the change in glass contact angle with time. After cooling, we sectioned the interface and analyzed it for evidence of reaction using electron microscopy and energy dispersive spectroscopy (EDS). The results typically show well-bonded interfaces with no evidence of Ni dissolution (the expected reaction mechanism) in the glass within the resolution of the measurement. In other experiments, we mixed up to 30 vol% Ni powder into different glasses and heated the specimens for up to 50 hours at 800°C as an extreme test of glass-Ni reactivity. Our most stable glasses showed no change in coefficient of thermal expansion after heating and no microscopic evidence for Ni dissolution.

Reactivity of glasses with interconnect materials was evaluated using the sessile drop method described above. Microscopic examination of interfaces showed no evidence of Cr dissolution (the most reactive constituent of stainless steel) or reaction products with the glass within the resolution of the technique. As an extreme test, we heated mixtures of glass and pure Cr powder at 750°C for increasing times. Similar to the case with stainless steels, no reaction products were observed at the interface, as shown in Figure 2. Since increasing temperature accelerates chemical reactions, we heated glass–Cr mixtures at 850°C. The results, as presented in Figure 3, showed that under those more extreme conditions, Cr reacts and dissolves in the glass. More work will be required to extrapolate the results for pure Cr and 850°C testing to realistic SOFC operating conditions and materials.

Preoxidizing 304 stainless steel housings used for electrical connectors has been shown to promote wetting and bonding with glass insulators. We extended those results by demonstrating that preoxidizing E-brite and 410 stainless steels is similarly beneficial for SOFC sealing (Figure 4). Heating the alloy at 1000°C for 5-30 minutes in Ar/1000 ppm O_2 produces a surface oxide layer 1-3 mm thick that is primarily Cr_2O_3 with a little SiO_2. Glass melted on the preoxidized alloy wets and adheres to the alloy in as little as 2 minutes, whereas reaching a steady-state contact angle on the bare

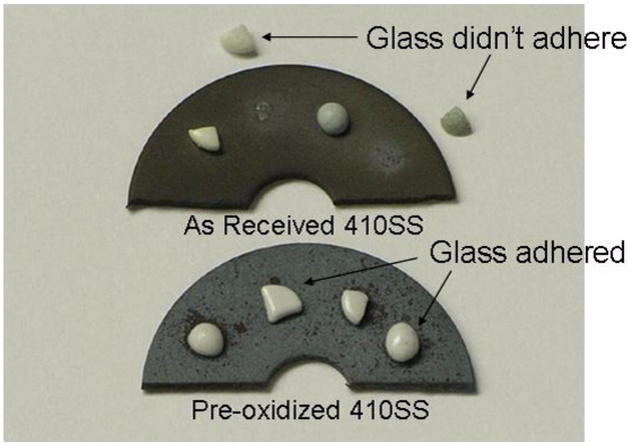

Figure 4. Glass Sealed at 850°C in Air Adhered Better to Preoxidized 410 Stainless Steel Than to the As-Received Form

alloy requires heating for 5 minutes or more. Minimizing time at the sealing temperature reduces the extent of undesirable interface reactions, so preoxidation of the interconnect may offer significant benefits in manufacturing SOFC stacks.

Conclusions

- Glass seal compositions provide excellent control over flow and thermal expansion properties.
- Seal compositions are stable in contact with anodes at 750-800°C and with stainless steel interconnect materials at 750°C.
- Preoxidizing interconnect materials offers advantages in SOFC seal processing.

FY 2005 Publications/Presentations

1. R.E. Loehman, et al., "Development of glass-ceramic composites for sealing solid oxide fuel cells", keynote talk, 29th Cocoa Beach conference, January 26, 2005
2. M. Brochu, B.D. Gauntt, D. Zschiesche, R. Shah and R.E. Loehman, "Development of glass/nano-ceramic composites for sealing solid oxide fuel cells", Ceramic Engineering and Science Proceedings, 2005
3. R.E. Loehman, "Materials challenges in the development of solid oxide fuel cells", invited seminar, Rice University, November 2004